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Pulsed-laser deposited ZnO for device applications

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Abstract

The study investigates the growth by pulsed-laser deposition (PLD) of ZnO thin films for the eventual incorporation into piezo-electric actuators and other sensors being developed at the University of Twente. All films are purely *c*-axis oriented, and results are presented which suggest the production of some of the highest quality ZnO thin films yet reported. These include films with rocking curve full-width half-maxima (FWHM) down to 1.2° and (002) 2θ peak FWHM (corrected) of 0.085°. Principally, X-ray diffraction analysis is detailed, and the shift in (002) peak position with changing deposition conditions is explored.

1. Introduction

ZnO is an n-type semiconductor which crystallises in the hexagonal wurtzite structure ($c = 5.2069$ Å, $a = 3.2495$ Å [1]). In bulk form, it has good piezo-electric properties, with d_{13} and ε_r equal to -5.0×10^{-12} C/N and 11.0, respectively [2]. Many different techniques, such as sputtering, chemical vapour deposition, ion-beam assisted reactive deposition, pulsed-laser deposition, chemical spraying, sol–gel and reactive evaporation have been employed in the growth of ZnO thin films. Of these techniques, sputtering has received by far the most attention and has been used to produce ZnO thin films with some of the best properties reported in the literature. These include a high degree of crystallinity, with the CuKα_1 (002) peak and rocking curve exhibiting full-width half-maxima (FWHM) as low as 0.198° and 1.6°, respectively [3], and optical transmittance as high as 99% [4]. Values of the resistivity of ZnO thin films, which may be altered by annealing [5] or doping with electron donor and acceptor elements [6–9], have been reported to vary by 17 orders of magnitude (10^{-4}–10^{12} Ω cm) and highlight the versatility of the material.

In this paper, the effects on pulsed-laser deposited ZnO thin films of deposition temperature and deposition rate are explored in more detail than previously, whilst the effect of the substrate type also is considered. Special emphasis is placed on XRD characterisations of the films, although results from spectrophotometry analyses also are presented. Additional characterisations using SEM, AFM, AES, ellipsometry and various electrical measurements will be detailed at a later date. It had been hoped to present initial results of the piezo-electric properties of these films. However, for the Si/Si–N/Al substrates currently available, excessive roughness of the sputter-deposited Al layer prevented these measurements at this time. These experiments must, of necessity, be

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deferred until better substrates are available. This latter observation serves as a particularly poignant example of the importance of the substrate surface morphology to thin film growth [10].

2. Experimental

Targets for PLD, ranging from 93–99% of theoretical density, are prepared from 99.99% pure ZnO

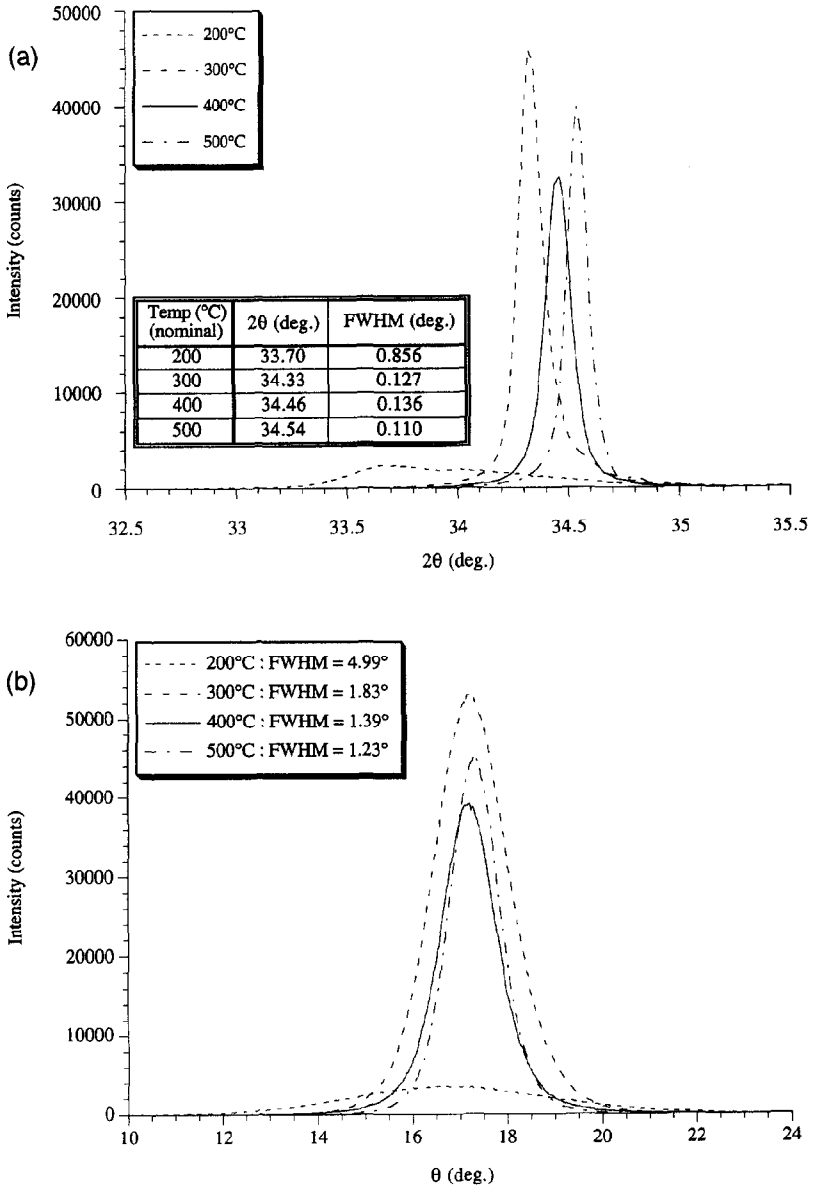

Fig. 1. ZnO films deposited onto quartz substrates at 5 Hz and different temperatures. (a) XRD (θ, 2θ) scans around (002) peak; (b) (002) rocking curves.

powder by cold-pressing (4 tonnes on 13 mm diameter pellet) followed by sintering for 12 hours at 1100°C in air. These targets are then placed in a rotating holder and ablated using a KrF excimer ($\lambda = 248$ nm) laser. The fluence of 5 J/cm^2 is kept constant for the experiments detailed here. The ablations are carried out with an oxygen background gas pressure of 1.3 mTorr [11] for periods of 5 to 50 minutes at pulse repetition rates of 2, 5 and 10 Hz. Four different substrate types have been employed, namely Corning 7059 glass, pure quartz (Spectrasil), Si (100) covered with its native oxide, and Si/Al at (nominal) deposition temperatures between 200°C and 500°C.

The use of 248 nm KrF excimer radiation for ZnO ablation was found in previous research to produce films of significantly higher quality than those grown using longer wavelength radiation [11–13]. Furthermore, ablation with 248 nm radiation leads to a smooth target surface after ablation [12] and, hence, all targets used here were pre-ablated prior to initial deposition, and not polished between depositions. XRD analyses were performed with a Philips PW3710 system.

3. Results

For the whole range of deposition parameters employed in this study, all the ZnO films were found by XRD to be c-axis oriented, exhibiting only the (002) and (004) XRD reflections. The effect of substrate temperature is explored in Fig. 1, in which XRD (θ, 2θ) and rocking curve scans of films grown on quartz substrates are shown. These films were grown at a laser repetition rate of 5 Hz and their thicknesses, as characterised by step profilometry, are 260, 310, 230 and 180 nm, for growth at 200, 300, 400 and 500°C, respectively. A dramatic improvement between 200 and 300°C is immediately apparent, whilst further, smaller improvements in (002) 2θ peak (Fig. 1(a)) and, particularly, rocking curve FWHM (Fig. 1(b)) continue to 500°C. The shape of the (002) 2θ peak after growth at 200°C is common to the films grown at low temperature, consisting apparently of two or more superimposed peaks, with an overall asymmetric distribution biased towards smaller c-axis spacings (e.g. [14]).

The increase in substrate temperature also leads to greater transparency of the thin film. Fig. 2 shows

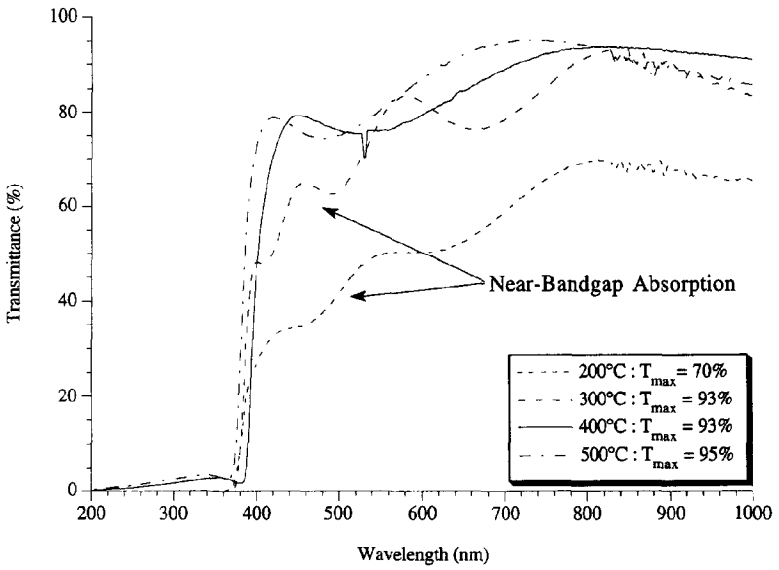

Fig. 2. Optical transmittance spectra from ZnO films deposited onto quartz substrates at 5 Hz and different temperatures.

spectro-photometry measurements in which the same series of films again exhibit a dramatic improvement in properties above 200°C, with transmittance attaining a maximum value of 95% for a film grown at 500°C. Whilst films grown at 300, 400 and 500°C all have very similar values for maximum transmittance, there is a noticeable improvement in transmittance for energies just below the bandgap on raising the substrate temperature during deposition from 300 to 400°C.

The film crystallinity is seen to be sensitive to deposition rate in Fig. 3. Here, films have been

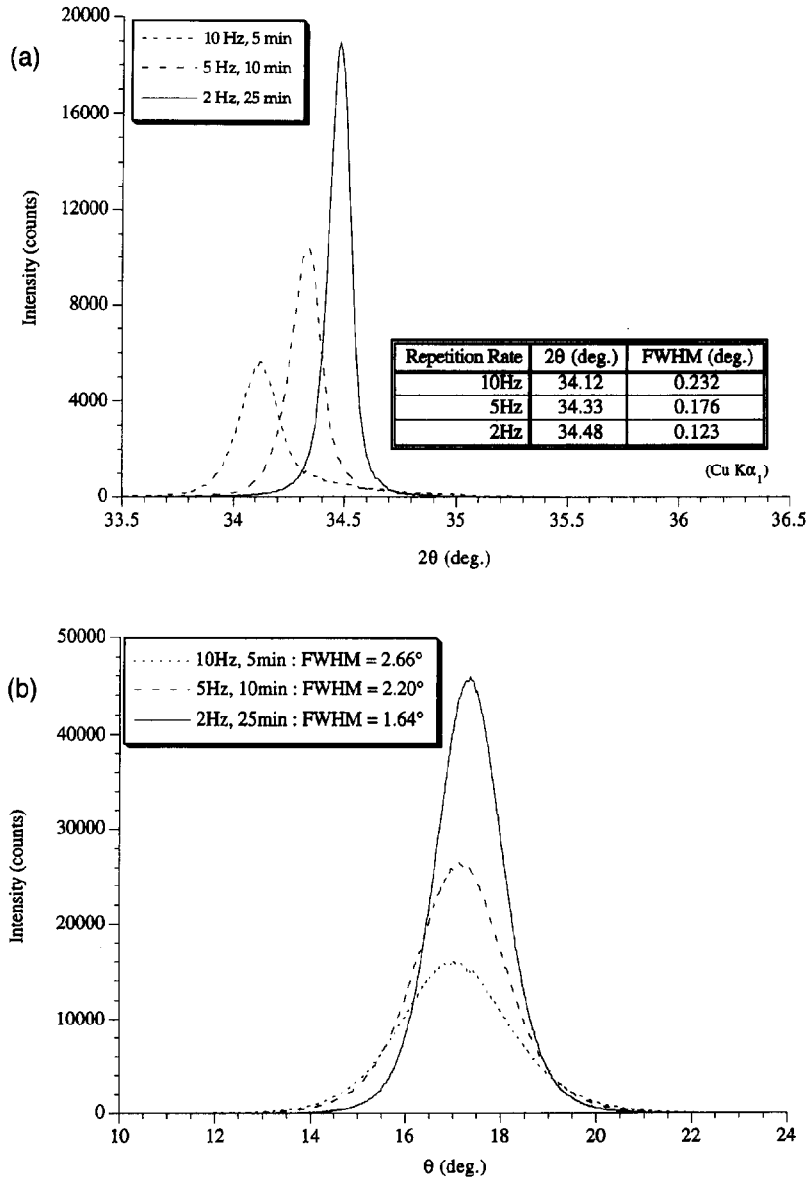

Fig. 3. ZnO films deposited onto Si/SiO_2 at 300°C and different repetition rates. (a) XRD (θ, 2θ) scans around (002) peak; (b) (002) rocking curves.

grown at laser repetition rates of 10, 5 and 2 Hz on Si substrates held at 300°C. The number of pulses was kept constant to yield film thicknesses of 272 nm, 289 nm and 255 nm (all ±5 nm), respectively, as characterised by ellipsometry and confirmed by step profilometry. Considerable improvement is seen in both (002) 2θ peak and rocking curve FWHM at lower deposition rates.

Figs. 1 and 3 both show the same trend. As film quality improves, evidenced by reduced FWHM, the

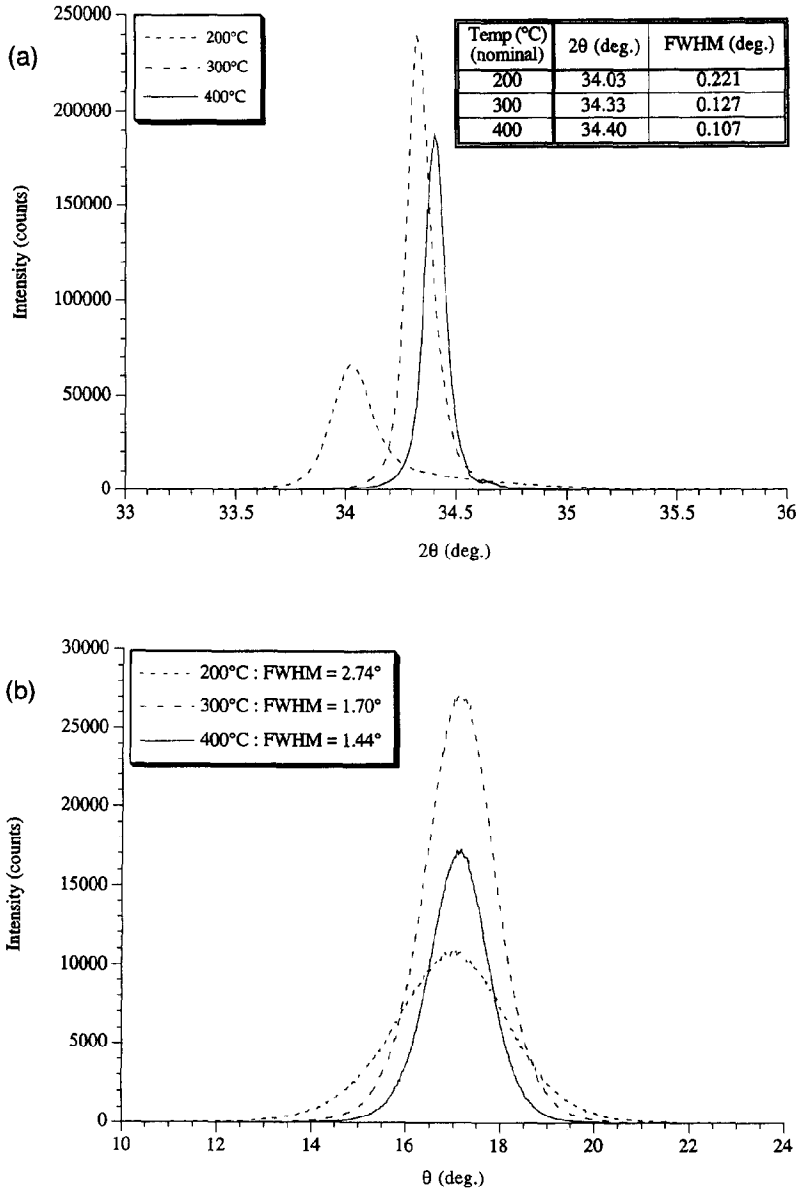

Fig. 4. ZnO films deposited onto corning 7059 glass at 5 Hz and different temperatures. (a) XRD (θ, 2θ) scans around (002) peak; (b) (002) rocking curves.

position of the (002) 2θ peak tends towards higher angles. This trend has also been seen for Si (covered with native SiO_2) substrates in earlier work [12]. One possible explanation which could be advanced for the shift in (002) peak position in Fig. 1(a) and in Ref. [12] is the introduction of macro-strain owing to a mismatch in thermal expansion coefficients (TEC) between substrate and film. ZnO has a TEC of 4 ppm/°C, whilst Spectrasil/SiO_2 has a TEC ~ 2 ppm/°C. The effect of this TEC mismatch would be to enlarge the ZnO a–b plane leading to larger (002) peak 2θ angles as the substrate and film are cooled from higher temperatures. Hence, this TEC mismatch would be in the correct sense to explain the above observations.

In Fig. 4, deposition onto Corning 7059 glass substrates is presented. All three films have similar thicknesses, namely 355, 310 and 385 (all ± 10) nm, for growth at 200, 300 and 400°C, respectively. Corning glass has a TEC of 4.5 ppm/°C. In common with the results of Fig. 1, and Fig. 3 of Ref. [12], improvement in film crystallinity with increasing substrate temperature is seen, as is a systematic shift in the position of the (002) 2θ peak. It is interesting to note that the value for 2θ (34.33°) is exactly (within diffractometer experimental error, which is 0.01°) the same for all films deposited at 300°C, whether deposited onto Corning Glass, Si(100) or quartz. This same value (or, 34.34°) has also been found for films of all thicknesses grown at 300°C (nominal) onto Al/Si and thick films (> 1 μm) grown onto Si/SiO_2. This precise agreement seems fortuitous bearing in mind possible experimental errors in temperature measurement, oxygen pressure, cooling rate and, to a lesser extent, laser fluence, but it may represent a fundamental characteristic of the growth and cooling process.

Data for the films grown at 500°C (Fig. 1(a)) and 400°C (Fig. 4(a)), which show the narrowest XRD 2θ line-widths, have been corrected approximately for instrumental broadening using the (004) peak from a Si substrate. This Si peak was then fitted to a pseudo-Voigt function to extract Lorentzian and Gaussian components (Voigt parameter $\phi = 0.8431$). Individual components were corrected for angle (69 to 34°) to a first approximation by assuming the Gaussian component was constant over this range, whilst the Lorentzian component scales as tan θ [15]. After fitting the ZnO (002) peaks in turn to a pseudo-Voigt function, corrected FWHM were extracted by direct subtraction for the Lorentzian component, and subtracting the squares of the Gaussian components. Substitution of the final values for both films into the Scherrer relation, yields average crystallite sizes of the order of 200 nm. This value has been reinforced qualitatively by cross-sectional SEM, in which single columnar grains appear to penetrate almost the entire film thickness.

4. Discussion

Results presented in this paper showing (002) peak and rocking curve FWHM down to 0.107° (uncorrected; when corrected for instrumental broadening, this becomes 0.085°, which is quite sufficient to resolve Cu $K\alpha_1$ and $K\alpha_2$ peaks at $2\theta = 34°$) and 1.23° represent ZnO films having some of the best crystalline properties yet reported for non-epitactic growth. These values are a significant improvement upon our earlier results [11,12], which were already the lowest values reported for non-epitactic growth of ZnO by PLD [8,13,16,17]. In fact, apart from two, quite exceptional, claims from Kyoto [18,19] for ZnO films sputtered onto glass exhibiting rocking curve FWHM down to 0.48°, the values given in this paper are the lowest of which the authors are aware for non-epitactic ZnO thin films grown by any technique. Furthermore, in a recent article [16], PLD has also been shown to yield extremely high quality epitactic ZnO thin films on sapphire substrates, with, as far as we are aware, the narrowest XRD linewidth yet reported for any ZnO thin film (rocking curve FWHM = 0.34°). Both observations bode well for the eventual application of pulsed-laser deposited ZnO thin films for, at this stage, small-scale device applications.

The 2θ peak position for (002) in bulk ZnO is 34.42° for Cu$K\alpha_1$ radiation. The phenomenon whereby the XRD 2θ (002) peak shifts with differing deposition conditions, initially from a position indicating tensile stress in the c-axis to one indicating compressive stress in the c-axis may be explained as follows. The possible effects of a mismatch in TECs between film and substrate are well known in thin film growth, and this mismatch has been known to cause cracking, buckling or complete

destruction of many specimens of different materials during cooling from high deposition temperatures. However, results presented here effectively rule out this effect as the only explanation for the observed peak shifting: The sense of the peak shift is constant for both quartz and Corning glass substrates, in spite of the fact that quartz would be expected to lead to a compressive stress on the c-axis, and Corning glass to a small tensile stress. The results for deposition at different rates onto Si/SiO_2 (Fig. 3) also rule out a TEC mismatch as the only explanation for the observed peak shifting, since, even if deposition rate is assumed to affect substrate temperature substantially (which would be a contentious assumption for PLD), the sense of peak shifting would require a significantly (~ 200°C) *lower* temperature at high deposition rates.

Instead, the observations may be explained as a combination of at least two effects, namely TEC mismatch and the annealing during growth of imperfections in the ZnO structure, such as stacking faults, grain boundaries and voids. Lattice imperfections and residual stress may be responsible for the absorption near the bandgap energy shown in Fig. 2 [20]. For films grown at 400°C and 500°C, this absorption is minimal, which suggests that a near perfect structure is in place for growth at 5 Hz and 400°C or more on quartz substrates. The removal of lattice imperfections has been advanced by Kim and Mathur [14] as a possible explanation for a shift in (002) peak position towards higher 2θ values after annealing, whilst such an affect also may explain other optical transmittance observations [21].

The XRD scans of Fig. 1(a) and 4(a) are qualitatively similar to those of Kim and Mathur, and, when taken in tandem with the observations of Fig. 2, certainly suggest that the presence or absence of lattice imperfections explains the generic shift, irrespective of substrate type, towards higher 2θ values with higher deposition temperature. The observations of Fig. 3, in which lower deposition rates lead to higher 2θ peak angles, also may be explained in these terms.

However, the above mechanism cannot explain a shift through the bulk value from tensile to compressive stress on changes in deposition conditions. Neither can the relaxation of interfacial stress advanced by Igasaki and Saito [22] as a possible explanation for similar observations in ZnO films sputtered on to sapphire substrates. In order to explain their observations, Igasaki and Saito suggest their diffractometer is in error, such that their upper value for the (002) peak position (34.61°) in fact represents the bulk value for ZnO (34.47° for poly-chromatic CuKα radiation). This issue could simply have been addressed by calibrating the apparatus using a substrate peak(s). Both our observations and those of Igasaki and Saito may be explained by considering the dual effects of TEC mismatch and lattice imperfections. As referred to above, the removal of lattice imperfections acts to move the 2θ peak position towards higher values, whilst, on Si/SiO_2, quartz or sapphire substrates, the TEC mismatch will tend to increase 2θ further, sometimes taking it above the bulk value. For the deposition at 400°C onto a Corning glass substrate, the slight TEC mismatch would act to reduce the 2θ peak angle below the bulk value, as observed. Hence, for a film deposited at elevated temperature, the final value for 2θ (002) arises from a combination of factors.

A final point concerning the position of the ZnO (002) peak in (θ, 2θ) scans relates to film stoichiometry. Gross deviations from ideal stoichiometry might be expected to introduce gross lattice defects. However, it is not impossible that small changes in stoichiometry, on the ppm level, also will influence the c-axis lattice parameter. Unfortunately, reliable data does not seem to be available here, perhaps owing to the extreme difficulty of sufficiently accurate (ppm) chemical analysis (also true of bulk samples), although an XRD study performed some time ago [23], apparently suggests that the magnitude of the effect will be small relative to those considered above.

Lastly, the observation that the 2θ angle ($= 34.33° \pm 0.01°$) remains constant for films deposited at 300°C and 5 Hz apparently suggests that any TEC mismatch is irrelevant under these deposition conditions. Such an observation might be explained by assuming that TEC mismatches only have a discernible effect when gross lattice imperfections (such as give rise to asymmetric XRD peaks or near-bandgap optical absorption) are not present; that is, under high temperature or low-rate deposition. Possible mechanisms by which this might occur are under investigation.

5. Conclusions

Pulsed laser deposition shows considerable promise for the deposition of very high quality ZnO thin films at low substrate temperatures. Considerable work remains to be done, since issues such as film resistivity and fundamental growth mechanisms remain to be addressed, but ZnO films deposited by PLD are expected to find eventual applications for the highest quality filters and actuators. Results presented here include films exhibiting (002) rocking curve and 2θ peak FWHM down to 1.23° and 0.085°, respectively, and grain sizes of the order of 200 nm. The shifting of (002) 2θ peak position as a function of deposition conditions (temperature and rate) and substrate is explained in terms of a thermal expansion coefficient mismatch and the presence or absence of lattice imperfections.

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